



The benefits of applying microsystems in radiochemistry

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Microsystems, in particular microelectromechanical systems (MEMS), are widely applied to the chemical analysis of fluids in pharmaceutical screening, biochemical assays, environmental monitoring, etc. The development of these microsystem applications is mainly economically driven: a series of experiments can be performed with a much smaller amount of material and with a much shorter preparation time. The chemical analysis of radioactive products is complicated by the necessary shielding to reduce the dose uptake for the analyst. For very 'hot' products with high radiation levels, either remote handling in hot cells with telemanipulators or extreme dilution is necessary. A radiochemist therefore uses different timescales for sample preparation and instrumentation setup. Nevertheless it seems that here also, a great benefit due to miniaturization can be expected. The scaling down of the radioactive sample means an almost proportional reduction of radiation, hence considerable simplification of the shielding measures. For sample size reduction by a factor of 1000, analysis of a real radioactive solution, for example a nitric acid solution in which spent nuclear fuel is dissolved, becomes possible in a glove-box system without the need for dilution.

Keywords: microsample, miniaturized spectrophotometry, radioactive solution

1. Background of microsystems carrying microchannel flows

1.1 Historical overview of the theoretical description of microchannel flow

Some 200 years ago, Young (1805) elaborated the structure of fluid films at boundaries at close range and observed that a surface tension exists not only at a gas/liquid interface, but also at a liquid/solid interface. He postulated that the three tensile forces (along the gas/liquid interface, solid/liquid interface and solid/gas interface) are arranged such that the horizontal components of the tension forces are in equilibrium. Despite the fact that Young's postulate has been

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questioned by Dussan & Davis (1971), and given an alternative interpretation with vanishing solid/gas tensile force by Janssens-Maenhout & Schulenberg (2003), Young's research formed the basis for thin-layer physics. Much more research was however required for the complete understanding of microchannel flow. In Young's times, the common understanding was that surface tension acts in a layer of zero thickness. On the other hand, no-slip as boundary condition was assumed for the fluid dynamic equation of Navier and Stokes. Consequently, single-phase capillary forces could not drive the flow.

By the end of the 19th century, van der Waals (1893) and Rayleigh (1892) had built up the statistical thermodynamic theory of a diffuse interface. Helmholtz (1879) was the first to realize that an electrode immersed in a solution of an electrolyte is surrounded by a zone of ions predominantly of opposite charge. Gouy (1910) and Chapman (1913) assumed that the underlying mechanism involved the opposing electric effects of the attractive Coulomb forces between the ions and the wall and the repulsive Coulomb forces between the ions themselves. Their theory characterizing these surface layers became known as the electric double layer (EDL) theory, which allowed capillary forces to influence or even dominate the flow through microchannels. Such flows in microchannels have been characterized² by Gad-el-Hak (1999) in microelectromechanical devices (MEMS) with sizes ranging from 1 mm down to 1 μm . The EDL field in such a microchannel, described by the two-dimensional nonlinear Poisson-Boltzmann equation, has been solved numerically by Mala, Yang and Li (1998) and analytically by Janssens-Maenhout & Schulenberg (2003).

1.2 Manufacturing microchannels allows practical use in MEMS

The practical use of microchannel flow in MEMS was enabled by significant progress in microfabrication techniques at the end of the 20th century. The common lithography and etch procedures of semiconductor integrated circuit (IC) manufacturing only produced microchannels of very limited depth. Combinations such as that used in the LIGA (X-ray lithography and galvano technique) process were needed to manufacture microchannels of sufficient depth for MEMS. An alternative became available with advanced micromilling to micrometre precision. In parallel, surface treatments such as thin-layer removal or coating (sputtering, evaporation, electroplating, cmp³ planarization, etc.) were introduced on an industrial scale.

In this way, the micromachining of T-microchannels, followed by the ultraprecise integration of electrodes or thin-layer coatings, led to various chemical analysis microsystems with embedded electro-osmotic pumps and valves, such as those developed by Manz et al. (1991). Still, a compromise is needed between the feasibility of manufacturing complex microchannel geometries and the desiredness of twisting fluid motion (resulting from the complex geometry) in the case of a micromixer, for which a two-dimensional (2D) concept is often not sufficient. A future method could use holography, in which a computer-generated hologram, placed as a mask at a minimum distance—the Fresnel length—from the substrate, yields after illumination the desired form for the MEMS. The last is of particular interest for

² Special caution is needed when averaging over characteristic lengths giving rise to microscopic effects, which invalidate the continuum approach in the limit of molecular length scales.

³ Chemical-mechanical polishing.

single-use microsystems, which are only affordable with cheap mass production. Instead of manufacturing a mould and stamping a (2D) microsystem in plastic by means of hot embossing, a hologram could be utilized many times as a mask, without losing its quality and guaranteeing the production of identical (2D and even 3D) microsystems.

2. Applying microsystems in radiochemistry

MEMS have been investigated as a means of analysing radioactive solutions in the nuclear reprocessing industry. Numerous applications can be found in e.g. nuclear safeguards, nuclear forensics, and nuclear medicine. At reprocessing plants with implemented safeguards, the total content of uranium (U) and plutonium (Pu) in the input and output accountancy tanks is accurately determined by taking a sample with several millilitres of solution for concentration measurements.

2.1 Example of a microsystem for the radiochemical analysis of spent fuel solutions

As a first step, it was proposed to replace the liquid sample in a typical 7 ml vial with a microlitre sample in a microchannel, which allows chemical analysis of the liquid in the microchannel by spectrophotometry. Through the channel, filled with the ionic solution by electrophoresis, a light beam is transmitted parallel with the axis, from the front side along the whole length. On the back side, positioned just opposite the light source on the front side, a spectrophotometer registers the wavelength-specific absorption of the light passing through the solution, which is characteristic of its composition. In order to guarantee that these spectrophotometric measurements are reliable and accurate, it has been necessary to investigate:

- i. Whether the radioactive (hot) solution distorts the microchannel volume by deformation or by radiochemical attack;
- ii. Whether the quantity of radionuclide in the microchannel solution is sufficient and homogeneously distributed over the channel for a reproducible measurement. This required the experimental derivation of the lower limit of radionuclide concentration in the solution.

Beside these two requirements, which are analysed with their underpinning experimental demonstrations in the following section (2.3), the microsystem needed to remain practical enough for use in a glove-box. A minimum size and an asymmetric form are necessary to facilitate the positioning of the microsystem between the light source and the spectrophotometer. To cope also with radioprotection measures, the microsystem needs to be sealed and leak-tight.

2.2 Realization of a first microsystem design for spent fuel solution analysis

A first prototype, manufactured in the workshop of the Politecnico di Torino, consisted of a Pyrex glass substrate 10 mm wide, 0.5 mm thick and 20 mm long, in which three microchannels of $300 \times 300 \mu\text{m}$ cross section and 18 mm length were fabricated using the powder blasting process.⁴ Fig. 1 shows the geometry. The first channel is the reference channel, containing neodymium nitrate lanthanide ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) solution⁵, which shows representative absorption peaks in the wavelength region of interest. The middle channel remains empty and

⁴ This implies the application of a metallic mask.

⁵ The actinides in the spent fuel solution show a lanthanide-like behaviour according to Seaborg et al. (1994).

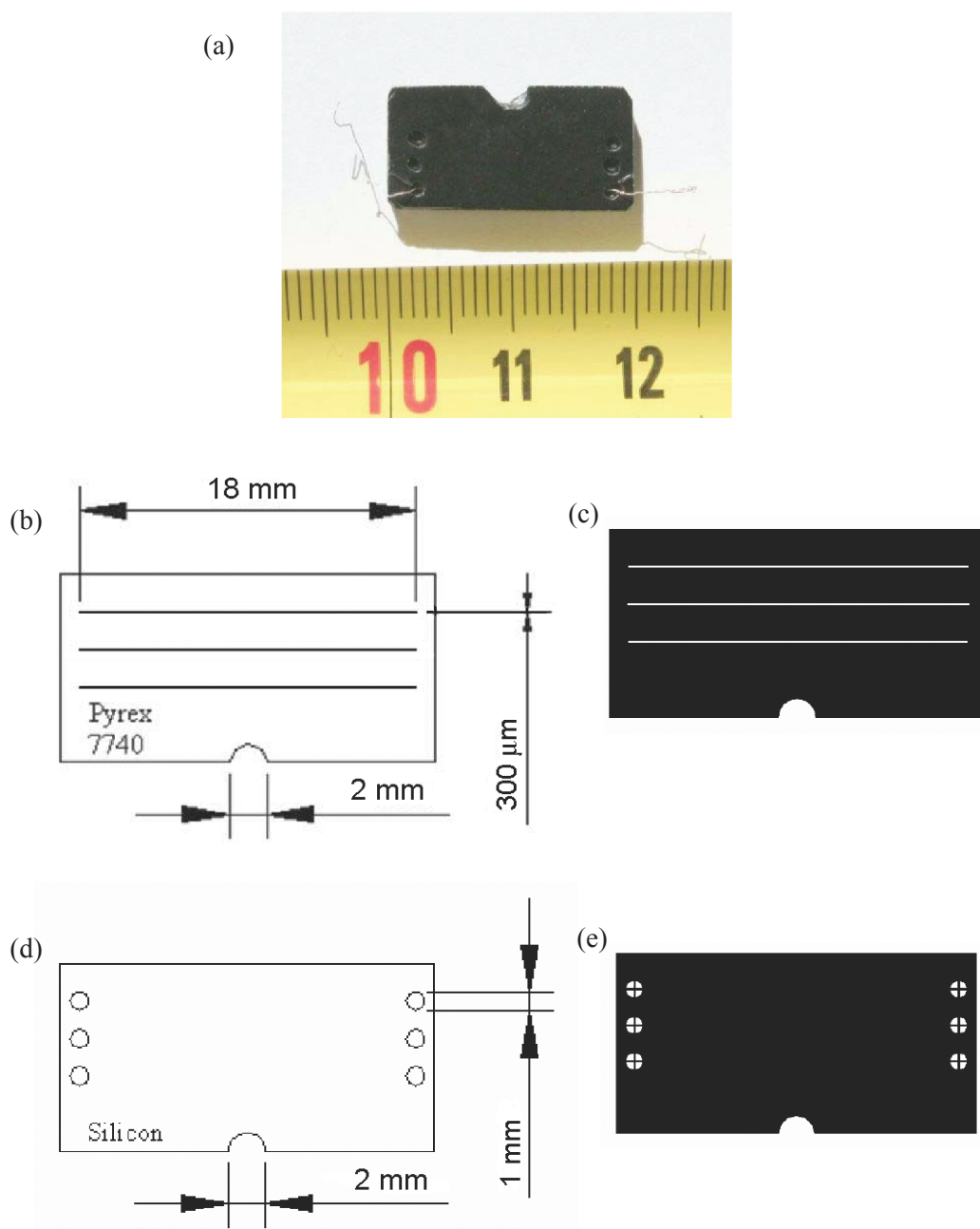


Figure 1. Microsystem with three microchannels for densitometric and spectrophotometric analysis of radioactive solutions. (a) Microsystem prototype in Pyrex glass with three identical microchannels ($300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ cross section) and covered with a silicon layer. In the first microchannel a copper wire simulates the hot radioactive solution. To facilitate the positioning of the microsystem one side is foreseen with a hole as locator. (b) Pyrex layout structure. (c) Mask for Pyrex powder blasting. (d) Silicon cap layout structure. (e) Mask for silicon powder blasting.

serves as an optical positioning channel. The third one is the chemical analysis channel, through which the radioactive solution of interest is pumped by applying the principle of electrophoresis.

The substrate is covered with a silicon layer 0.3 mm thick in which three cylindrical inlets and three outlets of diameter 1 mm are bored at the ends. Between the two layers, a series of electrodes are inserted to create the necessary electric field along the microchannel length axis for electrophoretic suction of the solution in a peristaltic fashion. The silicon cover was n/p doped and attached by an anodic bonding process to Pyrex glass (with a high sodium concentration). The complete microsystem was embedded in a positioning frame.

2.3 Theoretical feasibility study of a microsystem for the analysis of radioactive solutions

2.3.1 Material selection

The Pyrex glass, tightly bonded to the silicon layer, shows stable properties at high temperature and proved to be an ideal leak-tight testing device component. However, to cope with inspectorate requirements, single-use microsystems have to be envisaged, which must remain available for analysis for two months. Therefore, a second step is needed, namely to manufacture a mould with the negative form of the prototype, which is then used to emboss the tested prototype design in a polymer. High density polyethylene (HDPE) has been selected as the polymer because it is resistant to acidity and irradiation during the measurement interval, transparent for the spectrophotometry, and compatible with the material requirements for hot embossing. Moreover, radiochemists have confidence in HDPE because of the positive experience with this material over many years in the nuclear industry.

2.3.2 Thermodynamic and microfluidic analyses

Any thermo-fluid-dynamic simulation needs the density and viscosity of the radioactive solution as a function of the actinide concentration. The density and dynamic viscosity were measured with a precision of ± 1 g/l and ± 1 μ Pas respectively and have been tabulated for the reference solution of 3 M nitric acid with different Nd concentrations as a function of the temperature by Macerata et al. (2004). In addition, they give typical parameters for the nitric acid solutions in a Pyrex glass substrate, such as the Debye length, the surface charge, the dielectric constant, electric double layer potential and free surface tension, with which parameters the microfluidic simulations of the capillary inflow of the solution into the microchannel are carried out.

The flow in the microchannel is laminar and shows a fully developed Poiseuille profile 150 μ m from the inlet. The simulations indicated absence of any dead zone, which justifies the assumption that concentration profiles averaged over the cross section are representative. Fig. 2 shows the typical flow in one microchannel. The microchannel flow simulations have been documented in detail by Matthews et al. (2005).

Electrophoretic suction of the flow into the capillary with a velocity of 1 mm/s requires an external field of 19.8 V/mm. More details of the electro-osmotic mobility calculations have been reported by Macerata et al. (2004). This electric field was obtained by inserting 10 micro-electrodes successively paired with 50 V potential difference. The alternation of voltage between successive electrode pairs causes peristaltic inflow by electrophoresis.

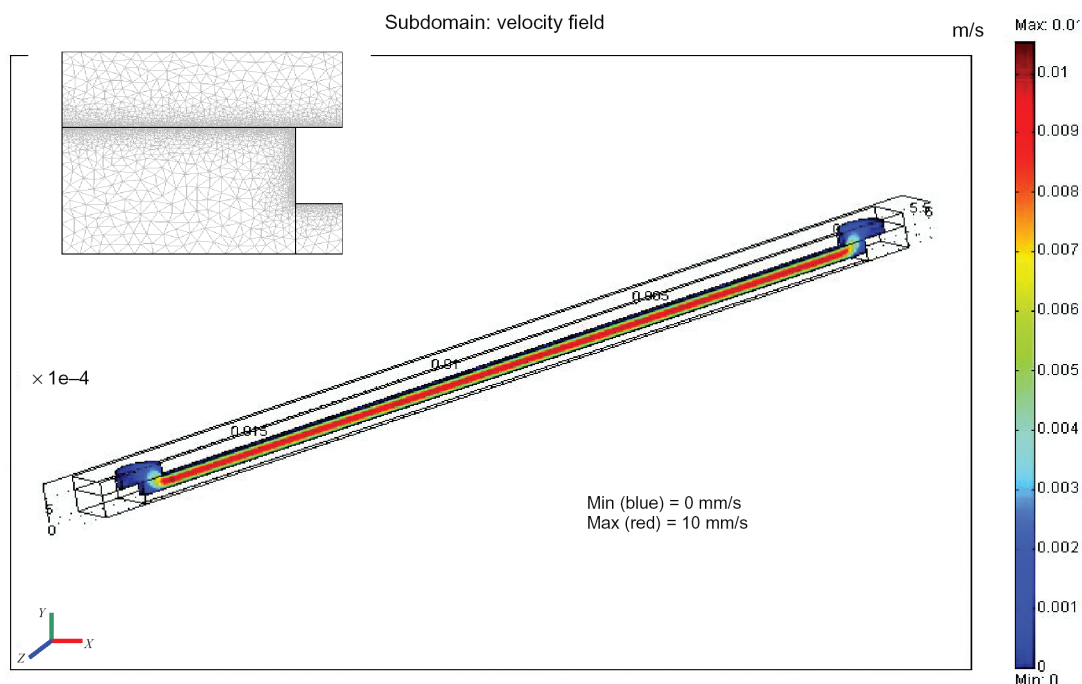


Figure 2. Microchannel flow simulation using the Finite Element Code COMSOL.

In order to evaluate the thermal stresses on the microchip induced by the radioactive and hot solution, thermodynamic simulations were combined with thermographical experiments by Uyttenhove (2005). The radioactive fluid can be considered as a thin heat source, which consists of the specific heat generated by the decay of the radionuclides in the solution. Only a heat source of the order of mW needs to be taken into account because of the microvolume containing this specific decay heat in the radioactive and therefore hot solution. The heat transfer from the hot microchannel fluid towards the ambient was modelled by conduction over the microchip material and with free convection at the outer chip wall. This was validated with thermographical measurements of the heat released from the prototype, in which copper wires simulated the hot solution at different powers. Fig. 3 gives the measured temperature increase for the power increasing from 0 mW to 250 mW. For a heat source of 50 mW, a maximum temperature difference of 5 °C was obtained between the initial and final temperatures of the microchip, with a steeper temperature gradient above the horizontal microchip because of the natural convection effect.

A realistic decay heat release of 1.5 mW induces a maximum temperature difference of only 0.5 °C. Even though this temperature variation is very small, the stresses on the microchip were evaluated. No deformation of the microchannel itself or of its position relative to the blank and reference channels can be allowed, because it would perturb the absorption spectra with a significant change in amplitude and shift the peaks towards other wavelengths. For a heat flux of 60 mW/cm² (corresponding to a 1.5 mW heat source) the temperature distribution in the microchip and the distribution of the stresses were numerically simulated for the prototype

Pyrex with silicon cover and for the single-use microchips made from HDPE. In both cases the von Mises stresses were largely below the maximum yield stresses and it was concluded that no Peltier cooling element was needed.

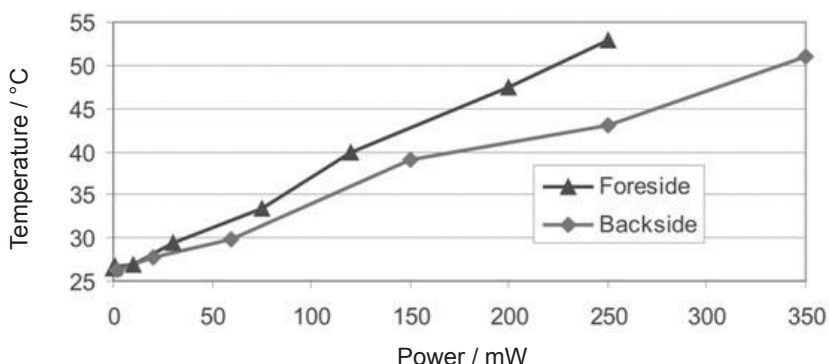


Figure 3. Average temperature measured at the surface of the microchip (in which a copper wire is inserted to simulate the radioactive solution heat source) by a thermographical camera for increasing power on the front side and on the back side.

2.3.3 Spectrophotometric analyses

The radioactive solution in this example is the spent fuel solution, or so-called input solution as collected in the input accountancy tank of a reprocessing plant. This input solution is typically prepared with 3 M nitric acid and the dissolved spent fuel, which contains typically from 2 g/l up to 250 g/l actinide nitrate. A photospectrometric reference database was set up with the measured absorption peak areas for typical aqueous solutions with different neodymium (Nd) concentrations.

Experimental proof of the possibility of spectrophotometric determination of the radioactive solution was given by Janssens-Maenhout & Nucifora (2007). The reproducibility and detection limits of the measured absorption spectra have been examined separately with the reference solution while downscaling stepwise the sample size and the path length. Fig. 4 shows the results for the 62 μ l cell. The experimental tests with a microsample of the neodymium nitrate reference solution demonstrated the feasibility of spectrophotometric concentration measurements in a validity range of 18 g/l to 230 g/l with the same accuracy as the standard measurements on the 7 ml vial. Moreover a high correlation factor (99%) was obtained representing the Lambert-Beer linearity between concentration and absorption peak area. The thermal liquid expansion and thermochromatic effects on the spectra led to a decrease in absorbance of less than 0.06% per degree of temperature and were therefore neglected. The influence of acid concentration on the spectra (3.8% per mole nitric acid per litre) was also kept negligibly small by standardizing the nitric acid samples to 3.0 ± 0.1 mol/dm³.

To anticipate problems with the real radioactive solutions, similar spectrophotometric analyses with real target solutions of $\text{UO}_2(\text{NO}_3)_2$ and $\text{PuO}_2(\text{NO}_3)_2$ in 3 M nitric acid were successfully carried out. The impact of potential impurities was investigated with 0.35 μ m silica particles added to the reference solution with a concentration of up to 1%. Their Rayleigh scattering effect on the spectra could be corrected for.

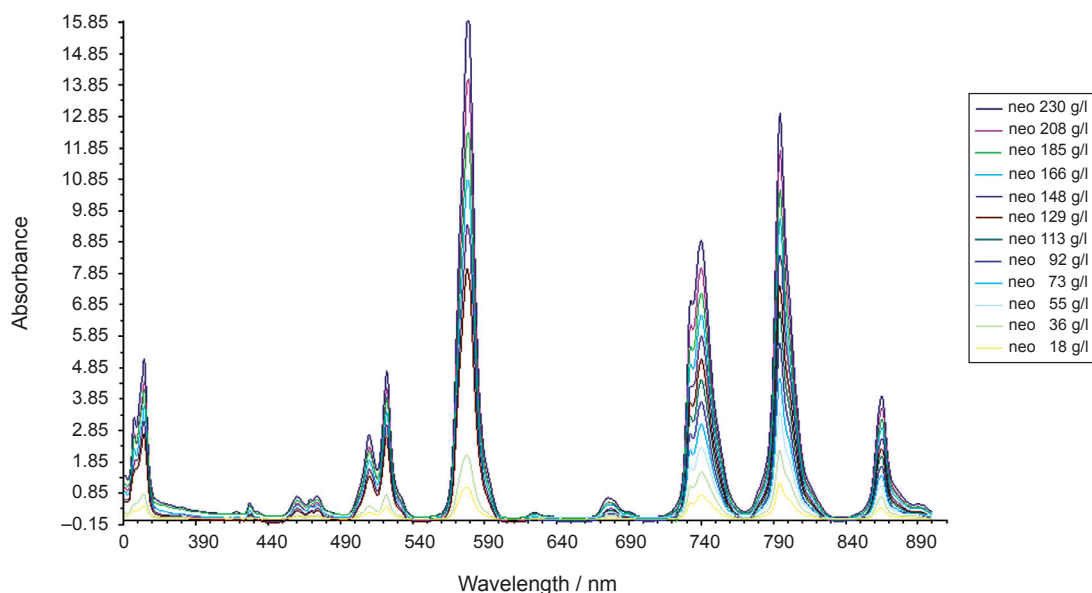


Figure 4. Absorption spectra for a 62 µl microsample of 3 M nitric acid with Nd at different concentrations (18–230 g/l).

3. Advantages of the microsystem for radiochemical analysis

The volume downscaling by three orders of magnitude in replacing the millilitre vial with a microlitre sample implies an almost proportional dose reduction. To comply with radioprotection measures, a conservative minimum dose reduction factor has to be derived. For the above example of the $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m} \times 18\text{ mm}$ microchannel for spent fuel solution analysis, the volume was reduced by a factor of 6320 and the mass of actinides in the solution by a factor of 6335 for high concentrations (250 g/l) up to a factor of 7000 for low concentrations (2 g/l). By means of Monte Carlo simulations, the minimum reduction in dose at a distance of 1 m was determined for different types of spent fuel dissolved in 3 M nitric acid. The dose reduction factor, expressing the gain in dose reduction for the most conservative case, was defined as the ratio of the lowest dose for the millivial to the highest dose of the microsystem caused by neutrons and photons.

For the different types of spent fuel, the dose reduction factor varies with at most 1% deviation around the averaged mean, which is given for the different concentrations of U-Pu spent fuel solution in Table 1. The results justify that a conservative lower limit for the dose reduction factor can be determined as 90% of the volume size reduction. Just 10% of proportionality is lost due to the change in self-shielding, mainly for the low energy gamma-rays. This decrease in self-shielding of the radioactive solution is explained with the increasing surface to volume ratio for the microsystem. More details are given by Janssens-Maenhout, Buyst & Peerani (2007).

The diminished radiation has several advantages. A direct analysis on the real solution can take place without dilution. This accelerates and simplifies the analysis procedure, and the results allow a direct interpretation with a smaller uncertainty range. The analysis can take place

Table 1. Conservative values for the reduction of the dose at a distance of 1 m from the microchip relative to the millivial as a function of the different spent fuel solution concentrations. The dose reduction factor has been averaged over different types of spent fuel (with different burn-up and cooling down times) and covers the individual spent fuel cases within a variation of 1% around this mean value. The last column represents the percentage of proportional dose reduction with volume size reduction.

[U-Pu] / g l^{-1}	U-Pu mass reduction	Conservative dose reduction at 1 m	Proportional volume reduction
2	7000	6019	95.2 %
25	6250	5962	94.3 %
100	6306	5873	92.9 %
250	6335	5807	91.9 %

in a glove-box system: no hot cell is needed any longer; and the reduction in shielding allows the analytical device to be transportable. The radioactive waste is also reduced, not only because of the minute volume of the microchip itself, but mainly because of the omission of the sample preparation. This means that the analysis is non-destructive and that the sample solution can be reintroduced into the process cycle.

This example provides experimental evidence for the feasibility and benefit of downscaling radioactive samples and miniaturizing analysis techniques in radiochemistry. Another example is under investigation in the area of environmental sampling, more particularly in the context of detecting undeclared reprocessing activities, using tributylphosphate (TBP) in the PUREX process. A miniaturized capillary electrophoresis system is applied to trace the TBP degradation products, dibutyl- and monobutylphosphate, in the microsample solution to which ytterbium-pyrocatechol is added as a colorimetric phosphor sensor.

Conclusions

This paper reports on research into the feasibility of applying a microchip for the chemical analysis of a radioactive solution. An example in the area of nuclear safeguards is given and shows experimental proof of the potential benefit of using microsystems in radiochemistry. This example demonstrated that:

- i. Manufacturing microchannels in the selected materials (Pyrex and high density polyethylene) is compatible with the geometry requirements of a straight channel with high aspect ratio;
- ii. Filling the capillary with the radioactive ionic solution is possible;
- iii. Concentration measurements by spectrophotometry of the wavelength-specific light absorption peaks are valid for microlitre samples;
- iv. Impact of the hot radioactive solution on the microchannel is negligible, with no potential to deform the channel and to perturb the absorption spectra;
- v. Radioprotection measures are significantly simplified even with a conservative dose reduction factor (90% of the volume size reduction factor).

The development of the example needed a multidisciplinary engineering approach and was possible thanks to a fruitful interaction with different research groups. Each discipline, from radiochemistry and neutronics to materials engineering and thermofluid dynamics, brought in distinctive requirements to the microsystem design. Moreover, the last two disciplines needed

to be applied with a different approach to model the thin layers, for which the well-known macroscopic laws become invalid.

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